Effect of substrate temperature on conductivity and microstructures of boron-doped silicon nanocrystals in SiC thin films

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HIGHLIGHTS
- SiC-matrix p-type Si-NCs were doped through the heavily B-doped CZ-Si target.
- Conductivity increased by 10–100 times when Ts was 200°C.
- Crystalline fraction increased by ~5% when Ts was 200°C.
- fcc Si-NCs formed in the surface layer when Ts was 200°C.

GRAPHICAL ABSTRACT

When Ts was ~200°C, crystalline fraction and conductivity of thin films increased, and fcc Si-NCs were formed in the surface layer.

ABSTRACT

Boron (B)-doped silicon-rich SiC (SiCx, 0<x<1) thin films were deposited using magnetron sputtering (MS) and annealed in a tube furnace. The effect of substrate temperature (Ts) on the conductivity and microstructures of the annealed B-doped SiC thin films were studied. The crystalline fraction increased by 5%, while the conductivity increased by 10–100 times, in the annealed thin films deposited at about 200°C comparing to that deposited at RT~400°C. The face-centered cubic (fcc) Si nanocrystals (Si-NCs) formed in the surface layer when Ts was about 200°C. It was suggested that Ts influenced the crystallization, conductivity and even the microstructures of Si-NCs. The proper Ts was helpful to improve the crystallization and conductivity of the B-doped Si-NCs in SiC thin film.

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1. Introduction

Silicon nanocrystals (Si-NCs) in Si-rich SiC (SiCx, 0<x<1) matrix have recently been interesting in photovoltaic [1] due to their inherent advantages (adjustable band gaps [2], strong multiple-exciton generation [3] and controllable array-growth structures [4] and low barrier of carrier transport [5]) for developing the next-generation solar cells [6–8]. Also, C coating may be good for the photovoltaic application of Si NCs [9,10]. The formation of Si-NCs in SiCx thin films usually includes two processes: the phase separation of amorphous silicon and the crystallization of amorphous silicon. Such processes are influenced by the composition and microstructure of the as-deposited thin films [11]. The composition and microstructure of as-deposited thin films will be influenced by the substrate temperature (Ts) during deposition [12]. Till now, many groups have studied Si-NCs in SiC thin films and have reported much valuable experimental studies about the formation of Si-NCs [13,14]. However, to our knowledge, the effect of Ts on the formation of Si-NCs in SiC thin films are scarcely investigated and remain unclear.

In this work, we deposited the boron (B)-doped SiCx thin films using different Ts and studied the effect of Ts on the crystallization,
conductivity and microstructures of the annealed SiC thin films. The as-deposited and annealed thin films were studied using Raman measurement, grazing incidence X-ray diffraction (GI-XRD), transmission electron microscopy (TEM), Hall measurements and atomic force microscopy (AFM). It was observed that the crystalline fraction of the annealed B-doped SiC thin films was highest when \( T_s \) was about 200 °C. Here, the annealed B-doped SiC thin films can be also named as Si-\( x \)-matrix B-doped Si-NC thin films, since the Si-NCs formed in the annealed thin films. The face-centered cubic (fcc) Si-NCs formed in the surface layer of the annealed SiC thin films when \( T_s \) was about 100–200 °C. The above results were probably related to the effect of \( T_s \) on the compositions of the as-deposited B-doped SiC thin films. The underlying mechanism was discussed.

2. Experimental

Quartz plates were used as the substrates, which were cleaned by standard wet chemical process. The B-doped SiC (0 < \( x < 1 \)) thin films were deposited using magnetron co-sputtering (J-sputter8000 magnetron sputtering system) of intrinsic polycrystalline SiC (4 N) and heavily B-doped Czochralski silicon (6 N). The resistivity of heavily B-doped Czochralski silicon was about \( 1.0 \times 10^{-3} \) \( \Omega \) cm; this resistivity corresponded to a B concentration of \( \sim 1.17 \times 10^{20} \) cm\(^{-3} \) [15]. The sputtering powers were 220 and 120 W for the Si target and SiC target, respectively. The sputtering powers were 220 and 120 W for the Si target and SiC target, respectively. The SiC thin films were deposited in the temperature range from RT to 400 °C. During deposition, \( T_s \) of the substrates range from room temperature (RT, \( \sim –20\) to 400 °C. After deposition the SiC thin films were annealed in a tube furnace at 1100 °C for 10 min [13,14,16,17]. The thin films were about 550–600 nm thick, as determined by a profilometer (Veeco Dektak 150). Chemical composition of the SiC thin films might be approximately denoted by Si\(_{0.75}\)C\(_{0.25}\), according to X-ray photoelectron spectroscopy (XPS, Kratos AXS ULTRADLD). The thin films were characterized by using a confocal micro-Raman spectroscope (Renishaw inVia) with the excitation of a Nd:YAG laser (532 nm). Grazing incidence X-ray diffraction (GI-XRD, Bruker AXS, D8 Discover, a voltage of 45 kV and a current of 40 mA, Cu K\(_\alpha\), radiation \( \lambda = 1.540562 \) Å) was employed to measure the annealed thin films at the incidence angle of 15°. A transmission electron microscopy (TEM) (Tecnai F20) was used to study the microstructures of the annealed thin films. The conductivity of the annealed thin films was determined by Hall measurements (Nanometrics HLS500PC). The surfaces of the as-deposited thin films were examined with an atomic force microscopy (AFM, CSPM5500 Scanning Probe Microscopy).

3. Results and discussion

The high-temperature annealing at 1100 °C leads to the crystallization of Si phase in SiC thin films [18–20]. The crystalline fraction of Si phase is derived from the Raman spectrum according to the accepted methods [21,22]. In general, the peak of Si phase is fitted using three peaks: 480 cm\(^{-1}\) (amorphous silicon), 510 cm\(^{-1}\) (nanocrystal silicon), and 520 cm\(^{-1}\) (crystal silicon) [21,22]. However, as shown in Fig. 1(a), the peak position of Raman TO-mode shifts to lower wave-numbers (\( \sim \) 515 cm\(^{-1}\)) for the crystalline Si film herein. The shift of peak position is probably due to a large tensile strain [23] or small grain size [24] in the nanocrystalline Si film. Raman spectra are analyzed with the software of XPSPK (version 4.1), which is developed for the division and fitting of peaks. The crystalline fraction of silicon is given by \( (I_{\mathrm{Si}}+h_{\mathrm{Si}}) / (I_{\mathrm{Si}}+h_{\mathrm{Si}} + I_{\mathrm{SiN}}) \), where \( \sigma \) is Raman emission cross-section ratio, \( I_{\mathrm{Si}} \) and \( h_{\mathrm{Si}} \) are the intensities of crystalline silicon, nanocrystal silicon and amorphous silicon. Fig. 1(a) shows the Raman peak of Si phase and its fitting lines in the annealed SiC thin film deposited at 200 °C. The dotted line denotes the experimental data. The solid lines result from fitting. Fig. 1(b) shows the crystalline fractions of the annealed SiC thin films deposited in the temperature range from RT to 400 °C. The crystalline fraction first increases and then decreases with the increase of \( T_s \). The crystalline fraction reaches the highest value (\( \sim 85\% \)) when \( T_s \) is 200 °C.

![Fig. 1](image.png)

Fig. 1. (a) Raman peak of Si phase and its fitting lines in the annealed SiC thin film deposited at 200 °C and (b) the crystalline fractions of Si phase in the annealed SiC thin films deposited in the temperature range from RT to 400 °C (1100 °C/10 min).
determined by Hall measurements. The activate energy of conductivity \((E_a)\) is extracted from the dependence of conductivity on temperature. Fig. 2(b) shows \(E_a\) in the annealed SiC thin films deposited at different \(T_s\). \(E_a\) reaches its lowest value when \(T_s\) is 200 °C. The above results suggested that \(T_s\) could significantly change the conductivity and \(E_a\) of the annealed SiC thin films. It should be mentioned that although B doping is an important issue, it is not discussed here. Since to determine directly the dopant location and efficiency by experiments is tremendously challenging in the nanometer-sized regime. The details of B doping can be refereed in the theoretical calculations \[25-28\].

The effect of \(T_s\) on the crystallization and conductivity of the annealed SiC thin films are discussed as following. It is known that \(T_s\) can provide the energy for the sputtering atoms during deposition. On one hand, increasing \(T_s\) can facilitate the Si–Si bonds and then the formation of crystalline Si clusters, which will act as the nuclei of Si-NCs and enhance the formation of Si-NCs. On the other hand, increasing \(T_s\) will also facilitate the formation of Si–C bonds \[29-31\]. Since the bonding energy of Si is higher in Si–C network than in Si–Si network \[32\], the diffusion barriers of Si should be higher in Si–C network than in Si–Si one. Hence, the formation of Si–C bonds in the as-deposited thin film would suppress the diffusion of Si and also suppress the crystallization of Si phase. The above analysis suggested that there was a proper range of substrate temperature which was useful to enhance the crystallization of SiC thin films. \(T_s\) at about 100–200 °C is useful for the crystallization of the SiC thin films.

Fig. 3 shows the GI-XRD spectrum of the annealed SiC thin film deposited at 200 °C. The three most strong peaks of the GI-XRD spectrum are located at 28.4°, 47.3° and 56.1°. According to the standard Joint Committee on Powder Diffraction Standard (JCPDS) cards, these peaks originate from the cubic-diamond (cd) silicon crystal. The cd Si has a lattice constant of 0.543 nm, in agreement with previous reports \[33,34\].

![Fig. 3. GI-XRD spectrum of the annealed SiC thin film deposited at 200 °C.](image)

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Fig. 2. (a) Conductivity, carrier concentration, carrier mobility, and (b) activation energy of the annealed SiC, thin films deposited in the temperature range from RT to 400 °C.

![Fig. 2.](image)

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Fig. 4(a) and (b) show the high-resolution (HR) TEM images and the selected area electron diffraction (SAED) pattern of the surface layer of the thin film. The lattice spacing of the Si crystal is about...

![Fig. 4.](image)
The reduction of the lattice spacing of the Si-NCs in the surface layer of the annealed thin films deposited at 200 °C is smaller than that of the as-deposited SiC thin films, as shown in Table 1. The corresponding lattice spacing and Miller index are listed in the table. This indicates that the formation of fcc Si-NCs in the surface layer was induced by the annealing process at high temperature. The lattice spacing of the fcc Si-NCs in the surface layer is given in Table 1, and the corresponding Miller indices are also listed.

<table>
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Fig. 5. AFM images of the surface morphology in the as-deposited SiC₃ thin films. (a) RT, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C.

4. Conclusions

The effect of Ts on the conductivity and microstructures of SiCₓ matrix B-doped Si-NCs thin films was studied. The crystalline fraction increased by 5%, while the conductivity increased by 10–100 times in the annealed thin film deposited at about 200 °C, compared to that deposited at RT–400 °C. It was suggested that the proper Ts was helpful to improve the crystallization and conductivity of the boron-doped Si-NC thin films. In addition, the annealed thin film deposited at ~200 °C usually had the fcc Si-NCs in the surface layer. The preferential generation of fcc Si-NCs was possibly related to the compositions of the as-deposited SiC₃ thin films.

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